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THE IONIZATION OF WATER, METHYLAMINE, AND METHYL ALCOHOL,  
USING ELECTRON AND ION IMPACT

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The ionization of water, methylamine, and methyl alcohol, using  
electron and ion impact.

By H. Sjögren

Abstract

The ionization of  $H_2O$  was investigated, using charge exchange in a double mass spectrometer. The breakdown graph was constructed. A break in the electron impact ionization efficiency curve is explained as being due to preionization, as its explanation as being due to an ion-molecule reaction between  $H^+$  ions and  $H_2O$  seems to be less probable. The appearance potential of  $OH^+$  was found to be considerably higher with charge exchange than when electron impact was used, which agrees with our earlier finding that intercombination transitions seem to be more strictly forbidden in charge exchange than in electron impact.

$CH_3NH_2$  and  $CH_3OH$  were investigated, using charge exchange at elevated pressures. The breaks in the ionization efficiency curves for these molecules are discussed and ascribed to preionization or secondary processes.

### Introduction

Our knowledge of the higher ionization potentials (IP) of small and large molecules has been rather limited hitherto. The IP's are calculated quantum-mechanically for a number of small molecules. Few comparisons with experimental results have been possible and have in some cases shown a discouraging lack of agreement. The high IP of methane was thus calculated to be about 25 eV, while the generally accepted experimental value was 19.4 eV. The third IP of water has been calculated to be 18.6 eV while experiments have given the value 16.2 eV. This lack of agreement has generally been interpreted as being due to considerable unreliability inherent in the quantum-mechanical calculations. In consequence the theoretical calculations on other molecules have also been considered less reliable.

This situation has now been changed. It has been possible to explain the discrepancies in the case of methane as due to ion-molecule reactions in the ion source of the mass spectrometers used [1, 2]. Experiments indicating a value of 24 eV have also been performed [2]. The good agreement between theory and experiment thus obtained shows that the theoretical calculations have reached a higher degree of reliability than previously was believed to exist, at least by experimentalists.

Ion-molecule reactions in the ion source have also been shown to give breaks in the electron impact ionization efficiency (IE) curves for  $O_2$  [3] and  $CO_2$  [4]. In this paper we will show that the earlier experimental value of the third IP of  $H_2O$  is not related to direct ionization, and that the correct experimental value is close to the theoretical value. The difference between

ion and electron impact processes will also be discussed.

We have also performed investigations on  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{OH}$  in order to see whether some discrepancies between the mass spectrometrically determined IP's and the ones determined by other methods can be explained in a similar way.

### The structure of H<sub>2</sub>O

The structure of water according to Mulliken [5] and Ellison and Shull [6], is given below, together with the IP's of the different electrons in eV.

	$1a_1^2$	$2a_1^2$	$1b_2^2$	$3a_1^2$	$1b_1^2$
Probable ionic state			$^2B_2$	$^2A_1$	$^2B_1$
IP's [6]	557	36	18.6	13.2	11.8
IP's [7]	560	36	18.5	15.1	13.4
IP's [8]			18.02	14.23	12.61

The IP's were obtained by LCAO-MO-SCF calculation [6, 7] and by photoelectron spectroscopy [8].

No potential energy curves for H<sub>2</sub>O seem to have been computed, although qualitative curves have been given by Schulz [9], Laidler [10], and Fiquet-Fayard [11, 12]. We have, therefore, tried to estimate the Franck-Condon factors for ionization of H<sub>2</sub>O from theoretical considerations and photoelectron spectroscopic measurements [13].

According to theoretical discussions [6, 14-16], the  $1b_1$  orbital is approximately nonbonding, the  $1b_2$  orbital is strongly bonding while the  $3a_1$  orbital is important for the angle between the OH bonds. Turner found evidence of at least three vibrational levels at 12.61 eV with a mean spacing of 0.4 eV. At 14.23 eV he found evidence that a strongly bonding electron is ionized, giving vibrations up to 17 eV. Finally, at 18.02 another strongly bonding electron is ionized, giving vibrations up to 20 eV. Since the  $3a_1$  orbital tends to diminish the angle between the OH bonds, ionization of this electron must lead to strong bending vibra-

tions. Therefore Turner's observations are in good agreement with theory.

By using this information we have approximately plotted the Franck-Condon curves in Fig. 1a. These curves give a picture of the probabilities for ionization when using electron and ion impact. No transitions to repulsive states are included in Fig. 1a, since these are not known, although they must also be taken into consideration. It was shown earlier ( $\text{CO}_2$  [4]) that the probabilities of these transitions are sometimes appreciable.

#### Molecular states of $\text{H}_2\text{O}$

Our knowledge of the excited states of the neutral water molecule has improved considerably during recent years. Walsh [15] has discussed the absorption of  $\text{H}_2\text{O}$  at 1655 Å and 1290 Å and has given reasons that both transitions go to a Rydberg state  $3sa_1$ , that is broadened owing to interaction with a repulsive  $a_1$  state. In the first case, the transition is due to a non-bonding  $1b_1$  electron, and in the second case a  $3a_1$  electron makes the transition. Therefore, in the last case bending vibrations are observed in the upper state. Owing to these vibrations, the energy of the  $3s$  state is best determined from the long wavelength absorption with maximum at 1655 Å, and can therefore be given as 5.1 eV below the ionization limit. The higher Rydberg levels  $4s$  and  $5s$  were observed by Price [17], and have recently been discussed by Johns [18]. They have energies 1.5 and 0.9 eV respectively, below the ionization limit. (The transitions measured by Johns are of minor interest owing to low intensity.)

Recently, Skerbele and Lassetre were able to observe all

these transitions by means of electron impact spectra [19]. Their results are given in Fig. 2. The high broad peak at 7.5 eV shows the transition  $1b_1 \rightarrow 3s$ . The transition  $3a_1 \rightarrow 3s$  starts at 9.1 eV, and the bending vibrations in the upper state make this peak very broad up to 10.4 eV. At 11.1 eV a very intense and narrow peak corresponds to the transition  $1b_1 \rightarrow 4s$ , and at 11.7 eV a small peak corresponds to  $1b_1 \rightarrow 5s$ .

Above the ionization limit in Skerbele and Lassettre's paper a very intense and broad peak can be observed. Since the excitation of an inner electron  $3a_1$  to  $3s$  gives a very intense peak in Lassettre's measurements, it is natural to suggest that the intense peak at 13 eV may be due to transitions of the inner electron  $1b_2$ . As Turner's new measurements have given the energy 18.0 eV for the  $1b_2$  electron, the energy of the transition  $1b_2 \rightarrow 3s$  can immediately be calculated as 12.9 eV. But it is further necessary to take into consideration that the  $1b_2$  electron is the main bonding electron in water according to Ellison and Shull [6], and that, therefore, very strong vibrations will be introduced on excitation of such an electron. It is, therefore, natural that the peak will extend from 12.9 eV up to 14 or 15 eV, which is in complete agreement with the results obtained by Skerbele and Lassettre.

As the transition at 11.1 eV ( $1b_1 \rightarrow 4s$ ) is nearly as intense as the transition at 7.5 eV ( $1b_1 \rightarrow 3s$ ), we expect that also the transition  $1b_2 \rightarrow 4s$  will be intense, and, owing to the vibrations, we will expect a broad peak between 16 and 17 eV. Such a peak is present in Fig. 2.

It is clear that a molecule in the state at about 16 eV will preionize, if a  $3a_1$  electron fills the hole in the  $1b_2$  orbital

(which is an allowed transition), and at the same time the 4s electron is ionized. In the state at 12.9 eV the molecule must have a small probability for preionization, for transition of a  $3a_1$  electron into the  $1b_2$  orbital does not give enough energy for preionization, and the transition  $1b_1 \rightarrow 1b_2$  must be weak. The state  $1b_2^2 3a_1 1b_1^2 4sa_1$  also at about 12.9 eV (not discussed earlier) can of course preionize as the transition  $1b_1 \rightarrow 3a_1$  is allowed and the energy is slightly higher than the ionization energy.

If there exists an excited neutral state of  $H_2O$  at 16 eV, this would be expected to appear by photoionization and photoabsorption measurements. Such investigations have been made by a number of authors. Astoin [20], Rathenau [21], and Henning [22] have found strong photoabsorption close to 16 eV. Metzger and Cook [23], on the other hand have found a minimum in their photoabsorption curve at this energy. The situation is therefore not clear.



Earlier electron impact investigations of  $H_2O$

Using photoelectrons, Price and Sugden [24] studied the total ionization of  $H_2O$  and found breaks in the IE curve at 12.6, 14.5, 16.2, and 18.0 eV. Schulz [9] and Sjögren [25, 26], using the RPD technique according to Fox et al. [27] and ionization chambers, found breaks at 12.6 and 14.5, and at 12.6, 14.2, and 16.2 eV, respectively. In addition, some of Sjögren's curves showed breaks at about 18 eV (unpublished). Using a mass spectrometer, Frost and McDowell [28] and Cottin [29] found breaks at 12.61, 14.35, and 16.34, and at 12.61, 14.5, and 16.1 eV, respectively.

It is evident that the first and second breaks in all these determinations correspond to ionization of the  $1b_1$  and  $3a_1$  electrons in good agreement with the previous values. Further, the break at 18 eV, obtained in some of the total ionization experiments, agrees well with Turner's value 18.02 eV for the ionization of the  $1b_2$  electron and also with the calculations by Ellison and Shull and by Moccia. In an earlier paper [2] Sjögren showed that especially Moccia's calculations of the high IP of methane [30] agree well with the new experimental determination of this IP. Since Moccia has performed the same type of calculations on water, a high degree of reliability must be ascribed to his values.

It therefore seems necessary to assume that the value at about 16.2 eV obtained in most of the electron impact experiments is not due to direct ionization but to a different process. This process must differ from the charge exchange described in the case of methane [1, 2] and  $CO_2$  [4], since the break is observed not only by mass spectrometry but also in the total ionization experi-

ments.

The electron impact mass spectrum of  $\text{H}_2\text{O}$  is given in Table 1 together with the appearance potentials (AP) [29, 31], possible dissociation limits, and the corresponding minimum energies. The minimum energies were calculated using known dissociation [32] and excitation [33] energies and the electron affinity of OH determined by Branscomb et al. [34]. Since the two  $\text{OH}^+$  states  $^1\Delta$  and  $^1\Sigma^+$  do not seem to have been detected spectroscopically, we have estimated their excitation energies in analogy to the similar states in the isoelectronic NH molecule [33] at 2 and 3 eV respectively. It may be remarked that the earlier value, 18.8 eV for the AP ( $\text{O}^+$ ), has been shown by Cottin [29] to be due to pressure induced metastable  $\text{OH}^+$  ions at mass 16.05. In addition, Cottin [29] found AP's of both  $\text{H}^+$  and  $\text{OH}^-$  at 16.0 eV indicating that these ions are formed in an ion-pair process at this energy.

However, these appearance potentials are not in agreement with the values calculated in Table 1. It is of course possible, that Cottin has an uncertain calibration of his energy scale and that the correct appearance potentials are 16.9 eV. Measurements by De Souza and Green [35], indicating that the AP ( $\text{OH}^-$ ) is 17.5 eV also support this point of view. In such a case, however, it is impossible to explain the formation of  $\text{H}_2\text{O}^+$  at 16.2 eV by means of the ion-molecule reaction involving  $\text{H}^+$  discussed below. On the other hand, it is possible that the theoretical calculation is inaccurate. The electron affinity of OH is still a matter for discussion, and also the dissociation energy of  $\text{H}_2\text{O}$  is somewhat uncertain.

In this situation there are evidently two possible ways of explaining the break at 16.2 eV in the electron impact experiments

Ion-pair formation and preionization. Both processes must at least in principle, give rise to breaks in the total ionization curves.

In order to explain the break at 16.2 eV by ion-pair formation, it is further necessary to assume that the  $H^+$  ions by subsequent charge exchange form new molecule ions according to



in analogy to what was found in the case of  $O_2$  [3]. That this is the case will be evident from our ion-impact investigations of  $H_2O$ . Although the recorded intensities of the  $H^+$  ions have been found to be low (Table 1) it must be remembered that these light  $H^+$  ions are discriminated in the mass spectrometer.

The possibility of preionization has been discussed above, and it was pointed out that the break would be situated near 16.2 eV. The energy of the break will thus be in better agreement with the observations than if ion-molecule reactions are considered.

### Ion impact investigations on $H_2O$

In order to investigate the ionization processes, we bombarded  $H_2O$  with slow positive ions in a double mass spectrometer described earlier [36, 37], and recorded the mass spectra. The results are shown in Table 2. The last column in the Table gives the relative cross sections (Q) in arbitrary units. The pressure of the target gas was determined by use of a Knudsen gauge. Unfortunately, the apparatus did not permit observation of  $H^+$ . Therefore the Q-values at high RE's are only lower limits.

In Fig. 1b the Q-values at high velocities are plotted. Evidently they are in good agreement with the estimated Franck-Condon factors in Fig. 1a. Bombardment with  $CO_2^+$ , recombination energy (RE) 13.8 eV [4, 36], thus gives approximately the same Q-values as with  $Kr^+$ , RE's 14.00 and 14.67 eV. This demonstrates the partly bonding character of the  $1b_1$  electron. It also shows that the charge exchange reaction (1) is allowed, since the lower RE of  $H^+$ , 13.6 eV, ought to give increased transition probability in comparison with  $CO_2^+$ . Also  $Ar^+$ , RE 15.8 eV, gives similar Q-values. The probability for ionization of the  $3a_1$  electron is therefore still large, 1.5 eV above the IP.

$F^+$  ions exist in three states,  $2s^2 2p^4 \ ^3P$ ,  $\ ^1D$ , and  $\ ^1S$  with RE's 17.42 ( $\ ^3P$ , 60%), 20.01 ( $\ ^1D$ , 30%), and 22.98 ( $\ ^1S$ , 10%) eV [3]. At low velocities, RE 17.42 eV gives no contribution to the mass spectrum according to Fig. 1a, while RE 20.01 eV gives  $H_2O^+$  predominantly in the stable  $\ ^2B_2$  state. RE 22.98 eV is only of minor importance due to the low abundance of the  $\ ^1S$  state and probably gives only  $OH^+$  ions from repulsive state. At high velocities translational energy enables the  $F^+ (\ ^1D)$  ions to trans-

fer more energy to the  $\text{H}_2\text{O}$  molecule. This explains the important velocity dependence in Table 2 since the  $\text{H}_2\text{O}^+$  ions will then be able to reach the dissociation limit of the  $^2\text{B}_2$  state and give  $\text{OH}^+$  ions according to Table 1. It is also possible that  $\text{H}_2\text{O}^+$  ions begin to form in repulsive states belonging to the same dissociation limit in Table 1. At the same time, the  $\text{F}^+$  ( $^3\text{P}$ ) ions will be able to ionize the  $^2\text{B}_2$  state, giving increasing absolute amounts of  $\text{H}_2\text{O}^+$  ions and increasing Q-values. Using  $\text{F}^+$  ions with 500 eV kinetic energy, Lindholm [38] obtained equal amounts of  $\text{H}_2\text{O}^+$  and  $\text{OH}^+$  ions.

$\text{Xe}^{++}$  ions have RE's about 12.5 and 18-20 eV, but formation of  $\text{Xe}^+$  through collisions above the collision chamber must also be considered at higher pressures [2].  $\text{Xe}^{++}$  gives similar velocity dependence as  $\text{F}^+$  ions, but extrapolation down to zero pressure and zero velocity shows that no  $\text{OH}^+$  ions form below 20 eV.

Using  $\text{Ne}^+$  ions, RE 21.6 eV, small Q-values are obtained in agreement with Fig. 1a. However, since the repulsive states leading to formation of  $\text{H}^+$  cannot be studied in the present experiment, these Q-values are only lower limits. Evidently the  $\text{OH}^+$  ions are predominating at low pressures.

When the pressure is increased, the relative abundances of  $\text{H}_2\text{O}^+$  increase, when bombarding with  $\text{Ne}^+$ ,  $\text{F}^+$ , and  $\text{Xe}^{++}$ , probably according to reaction (1) or to



which also is energetically possible. Extrapolation down to zero pressure must therefore be performed and shows in the case of  $\text{Ne}^+$  that the  $\text{H}_2\text{O}^+$  ions are unstable at 21.6 eV. This is very interesting because together with the  $\text{F}^+$  and  $\text{Xe}^{++}$  results above it shows that the AP of  $\text{OH}^+$  seems to be much higher when using charge

exchange than when electron impact is used.

In Fig. 1c a tentative breakdown graph of  $\text{H}_2\text{O}^+$  is plotted, using the results from Table 2 and the AP's discussed above. This graph gives but little information about the dissociation above 19.5 eV because of the unknown amounts of  $\text{H}^+$  ions. Since  $\text{H}^+$  must be formed from repulsive states, it seems likely that the abundances of  $\text{H}^+$  at 20 eV are still low. This is consistent with the fact that no further breaks seem to have been reported above 18 eV in the mass spectrometrically determined IE curve of  $\text{H}_2\text{O}$ .

$\text{H}^+$

### A theoretical discussion of the dissociation of $\text{H}_2\text{O}^+$

The dissociation of  $\text{H}_2\text{O}$  has been the subject of many theoretical and experimental investigations [11, 12, 39-43]. On the other hand, the dissociation of  $\text{H}_2\text{O}^+$  has been the subject of only a few theoretical investigations [10-12] performed by means of a generalization of the Wigner-Witmer correlation rules. In this way it was possible for Fiquet-Fayard to draw the potential energy curves for  $\text{H}_2\text{O}^+$  approximately (ref. 12, p. 459). We will accept the main features of her diagram with a few minor exceptions. Firstly, it must be corrected for the new experimental IP of the  $^2\text{B}_2$  state, and, secondly, we think it is necessary to include  $\text{OH}^+ (^1\Delta)$  and  $\text{OH}^+ (^1\Sigma)$  amongst the dissociation products, although these states have not yet been observed by the spectroscopists (Table 1) (cf. [33]).

In view of the results and discussions above it is evident that formation of the  $^2\text{B}_1$  state by means of ionization of a  $1b_1$  electron will not be followed by dissociation; this electron is essentially nonbonding. The  $^2\text{B}_1$  state is, therefore, stable.

Nor will formation of the  $^2\text{A}_1$  state by means of ionization of a  $3a_1$  electron cause any dissociation. The HOH angle will increase considerably and the  $^2\text{A}_1$  state is probably linear (cf. the corresponding state of  $\text{NH}_2$ , which has been proven to be linear [44]). The  $^2\text{A}_1$  state will therefore be formed with vibrational excitation, but will also be stable.

When the  $^2\text{B}_2$  state is obtained after ionization of the bonding  $1b_2$  electron it is necessary to distinguish between high and low vibrational energy of the state. As the  $1b_2$  electron is bonding [6] both cases are possible. In the first case the  $^2\text{B}_2$  ion is formed with low vibrational energy. It is then perfectly stable,

although it is energetically higher than the dissociation limit at 17.9 eV, since predissociation is forbidden for reasons of symmetry. However, this rule no longer holds in a collision with a gas molecule, and pressure induced metastable  $\text{OH}^+$  ions, probably formed in this manner, were observed by Cottin [29]. In the second case dissociation takes place as soon as the energy exceeds the dissociation limit  $\text{OH}^+ (^1\Delta \text{ or } ^1\Sigma) + \text{H}$ . The AP of  $\text{OH}^+$  is therefore expected to be about 21 eV, in perfect agreement with our results that for ions with  $\bar{E}$  lower than 20.0 eV no  $\text{OH}^+$  ions are obtained.

Using electron impact, the lowest AP of  $\text{OH}^+$  has been found to be 18.1 eV [29] in disagreement with theory and with our ion impact results. The explanation must probably involve the repulsive state  $^4B_1$  or  $^4A_2$ , correlating with the dissociation limit  $\text{OH}^+ (^3\Sigma^-) + \text{H}$  at 17.9 eV. The quartet state can be formed either directly in the electron impact or via a preionizing neutral triplet state. Evidently these results imply that intercombination transitions, which seem to be forbidden in charge exchange, can be of importance in electron impact. The results on  $\text{H}_2\text{O}$  are similar in this respect to our results with  $\text{CO}_2$  [4].

The next repulsive state ( $^2B_1$  or  $^2A_2$ ) correlates with the dissociation limit  $\text{H}^+ + \text{OH} (^2\Pi_1)$  at 18.7 eV, but all other repulsive states go to limits higher than about 20 eV and are therefore without interest in connection with our discussion of the formation of  $\text{OH}^+$  below 20 eV.

The fragmentation of  $\text{H}_2\text{O}^+$  giving  $\text{O}^+$  and  $\text{H}_2^+$  has also been treated theoretically by Fiquet-Fayard [11, 12] and experimentally by Cottin [29]. It will not be discussed further in this paper since no  $\text{H}_2^+$  ions can be observed in our apparatus and the AP of  $\text{O}^+$  is higher than 29 eV [29].



The structures of  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{OH}$

The structures of  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{OH}$  have been given by Mulliken [45] and were further discussed in earlier papers from this laboratory [37, 46]. They are given below for reference together with earlier and new estimations of the IP's in eV. The changes that have been made are discussed below.

$\text{CH}_3\text{NH}_2$	$1s^2$	$1s^2$	$2s^2$	$2s^2$	$z^2$	$x^2$	$y^2$	$z^2$	$x^2$
Location	N	C	$\text{NH}_2$	$\text{CH}_3$	$\text{NH}_2$	$\text{CH}_3$	CN	$\text{CH}_3$	N
IP, earlier [37]				19.89	16.57	15.07	13.94	12.16	9.18
IP	421	304	30	24	16.57	15.07	13.94	12.16	9.18
Mulliken [45]			(27)	(22)	16	14.5	13.5	14.5	11
$\text{CH}_3\text{OH}$	$1s^2$	$1s^2$	$2s^2$	$2s^2$	$z^2$	$x^2$	$y^2$	$z^2$	$x^2$
Location	O	C	OH	$\text{CH}_3$	OH	$\text{CH}_3$	CO	$\text{CH}_3$	O
IP, earlier [46]				19	15.3	15.0	13.1	13.0	10.9
IP	557	304	36	24	17.23	14.64	14.64	12.33	10.83
Mulliken [45]			32	22	17.5	14.5	16	14.5	12.5

As the two isoelectronic molecules are very similar and have nearly identical breakdown graphs [37, 46], similar coordinate systems have been chosen for their representation. From the designation of the orbitals the interaction between different orbitals is immediately clear.

In  $\text{CH}_3\text{NH}_2$ , the IP of the  $\text{CH}_3$  bonding  $2s$  electron has been changed to 24 eV in accordance with the value obtained by Sjögren for the corresponding IP in methane [2]. In agreement with the discussion in [37] the lower IP's have been taken from photoelectron spectroscopy measurements by Turner [8] and the higher values are taken from Meccia's quantum-mechanical calculations

for  $\text{CH}_4$  [30] and  $\text{NH}_3$  [47]. In this way, one of the values given by Turner (19.89 eV) has not been used. Since it was put in parentheses by Turner it is probably dubious.

In  $\text{CH}_3\text{OH}$ , the IP of the  $\text{CH}_3$  bonding  $2s$  electron has been changed to 24 eV for the same reason as in  $\text{CH}_3\text{NH}_2$ . The values for the IP's of the O ( $1s$ ) and the C ( $1s$ ) orbitals are taken from Meccia's calculations for  $\text{H}_2\text{O}$  [7] and  $\text{CH}_4$  [30]. The earlier IP of the OH [ $z$ ] orbital was estimated as the mean of the second and third IP of  $\text{H}_2\text{O}$ . This third IP has now been shown to be 18 eV, which gives the mean value 16.1 eV. Interaction with the  $\text{CH}_3$  [ $z$ ] orbital of the same symmetry is probably strong enough to elevate the IP further to reach Turner's value at 17.2 eV, at the same time as the  $\text{CH}_3$  [ $z$ ] orbital is depressed by about the same amount to around 12 eV. The assignment to the lower IP's is complicated by the fact that Turner has found one IP too few in  $\text{CH}_3\text{OH}$ . In lack of further data the same value has therefore been assigned to the CO [ $y$ ] orbital and the  $\text{CH}_3$  [ $x$ ] orbital at 14.6 eV. It is of course possible to assume that the IP of the CO [ $y$ ] orbital would be 12.3 eV. However, with such an assignment, the IP of the CO orbital would be much lower than the IP of the CN orbital. In consequence, it would therefore seem necessary to assume that in  $\text{CH}_3\text{NH}_2$  the IP's of the CO [ $y$ ] and the  $\text{CH}_3$  [ $z$ ] orbitals have the same value 12.16 eV, and that also the value 13.94 eV must be disregarded, which is less probable.

It is possible that photoelectron spectroscopical measurements with increased resolution will solve some of these problems. It is remarkable how well the IP's obtained in this way agree with the old estimations by Mulliken in Journal of Chemical Physics 3, 506 (1935), except that Mulliken did not take the interaction of the  $\text{CH}_3$  orbitals with the other orbitals into consideration.

### Earlier measurements

Using electron impact and an ionization chamber, Sjögren [26] has studied the IE curve for  $\text{CH}_3\text{OH}$ . Breaks in the IE curve for  $\text{CH}_3\text{OH}$  were found at 10.8, 11.7, 12.6, and 14.3 eV in reasonable agreement with the IP's above, except for the value 11.7 eV. Similar measurements on  $\text{CH}_3\text{NH}_2$  will be described below.

Using electron impact and mass spectrometric analysis Collin [48] measured the IE curves for  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{NH}_2$ . In the  $\text{CH}_3\text{OH}^+$  curve breaks appeared at 10.85, 12.82, 14.5, 16.06, and 18.85 eV, and in the  $\text{CH}_3\text{NH}_2^+$  curve the breaks appeared at 9.45, 12.35, 13.90, 17.70, 21.75, and 23.75 eV.  $\text{CH}_3\text{OH}$  has also been investigated with a similar technique by Tsuda and Hamill [49] who found breaks at 10.85, 11.1, 12.1, 13.2, and 13.7 eV.

Using photoabsorption, Sanson et al. [50] obtained the IP's 14.3 and 17.6 eV for  $\text{CH}_3\text{OH}$  in good agreement with Turner's values.

The ion impact mass spectra of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{NH}_2$  have been studied by Wilmenius and Lindholm [46] and Sjögren [37]. It was found that the  $\text{CH}_3\text{OH}^+$  ion rapidly dissociates having received energies above 12 eV, and that the  $\text{CH}_3\text{NH}_2^+$  ion is stable only up to 10 eV. In view of these results it is difficult to understand how the breaks in the mass spectroscopically determined IE curves are obtained.

### Experimental results

In order to investigate whether the mass spectroscopically determined breaks may be due to preionization or to a charge exchange mechanism of the same type as was observed in  $\text{CH}_4$  [2] and  $\text{CO}_2$  [4], the following experiments were performed.

$\text{CH}_3\text{NH}_2$  was bombarded with quasi-monochromatic electrons in an ionization chamber and the total ionization curve was measured at an estimated pressure of  $10^{-4}$  torr. The apparatus has been described earlier [2, 26]. The energy scale was calibrated using the resonance capture peak of  $\text{CH}_3\text{NH}_2$  which was measured simultaneously with the positive ion curve. This peak was found to have a narrow maximum at 5.4 eV. The position was determined using different mixtures of  $\text{CH}_3\text{NH}_2$  and  $\text{H}_2\text{O}$ . The latter molecule has a resonance capture peak at 6.6 eV determined earlier [51] in agreement with results by Buchelnikova [52] 6.4 eV and Schultz [9] 6.5 eV. The difference between the two peaks was found to be 1.2 eV.

Breaks in the positive ion curve of pure  $\text{CH}_3\text{NH}_2$  were observed at  $9.0 \pm 0.1$ ,  $9.5 \pm 0.1$ , and  $9.9 \pm 0.1$  eV (mean of 8 runs). The AP is therefore 9.0 eV in good agreement with the spectroscopic value 8.97 eV of Watanabe [53]. Additional breaks were observed at  $10.3 \pm 0.1$  eV (6 runs) and  $10.8 \pm 0.3$  eV (5 runs). No reproducible breaks at higher energies were obtained. The breaks must be ascribed to preionization or to excitation of vibrational states.

$\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{NH}_2$  were further investigated by means of charge exchange at elevated pressures in a double mass spectrometer. A Knudsen gauge was used to determine the pressures.

The relative abundances of the molecule ions after charge exchange with slow positive ions are shown in Table 3. The spectra

were resolved into mono-isotopic peaks and the sums of the peak heights were normalized to 100.

The molecule ions in Table 3 are no doubt formed in secondary processes, but evidently the small increase is insufficient to explain the breaks in the IE curves as being due to charge exchange between fragment ions formed after the primary charge exchange and the parent gas. The behaviour of the ions "parent-plus-one" shows, however, that ion-molecule reactions do occur in the collision chamber.

A further possibility, that cannot be investigated using this method, is that the fragment ions that might be responsible for the electron impact results are obtained through ion-pair formation. Since  $\text{CH}_3^+ + \text{OH}$  appears at 13.7 eV [49] and since the electron affinity of OH is 1.8 eV [34, 49] one may assume that  $\text{CH}_3^+ + \text{OH}^-$  appears at 11.9 eV. This is also verified by experiments [49], and may explain the break at 11.7 eV in Sjögren's IE curve for  $\text{CH}_3\text{OH}$  [26]. No corresponding break would be obtained in a mass spectrometrically determined IE curve, since the RE of  $\text{CH}_3^+$  is too low, 9.8 eV [37], but, in spite of this, Tsuda and Hamill obtained a number of breaks in their curve for  $\text{CH}_3\text{OH}$  at energies below 13.7 eV. It is therefore impossible to decide whether the break is due to ion-pair formation, preionization, or, perhaps, vibrational excitation.

To explain the break found by Collin at 12.35 eV in  $\text{CH}_3\text{NH}_2$  a similar discussion can be carried through. Since  $\text{CH}_3^+ + \text{NH}_2$  appears at about 13.9 eV and since the electron affinity of  $\text{NH}_2$  is about 1.2 eV [54] the appearance potential of  $\text{CH}_3^+ + \text{NH}_2^-$  can be calculated to be 12.7 eV. In this case charge exchange is allowed because of the low AP of the  $\text{CH}_3\text{NH}_2^+$  ion, and it is therefore natural that the pressure dependence is more pronounced for this

ion than for the  $\text{CH}_3\text{OH}^+$  ion (Table 3). However, since the electron impact measurements have shown a number of breaks below 12 eV and since the abundance of  $\text{CH}_3^+$  ions is low in the mass spectrum of  $\text{CH}_3\text{NH}_2$ , it must be concluded that also in the case of  $\text{CH}_3\text{NH}_2$  this process is a less likely reason for the low energy breaks.

The breaks at higher energies for both molecules may, in addition, be explained by charge exchange reactions between parent gas and fragment ions with higher RE's formed from molecular or ionic states that are not possible to reach by ion bombardment (cf. the discussion of  $\text{H}_2\text{O}$ ). In this case it is, of course, not possible to investigate the reactions by ion bombardment.

Regardless of whether the breaks in the electron impact IE curves for  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{NH}_2$  thus are caused by charge exchange, or by preionization, it is evident that they cannot be used to determine the higher ionization potentials of the molecules without further analysis. The agreement with independently measured IP's seem, therefore, to be accidental.

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Table 1. Electron impact mass spectra of  $\text{H}_2\text{O}$ , AP's in eV,  
dissociation limits and minimum energies in eV.

Ion	Electron impact mass spectrum				Possible processes	Minimum energy
	Mann et al. [24] Cottin [22]					
	MS <sup>a</sup>	AP's	MS <sup>b</sup>	AP's		
H <sub>2</sub> O <sup>+</sup>	100	13.0	100	12.6	H <sub>2</sub> O( <sup>1</sup> A <sub>1</sub> ) → H <sub>2</sub> O <sup>+</sup> ( <sup>2</sup> B <sub>1</sub> )	-
OH <sup>+</sup>	23.2	18.7	23.0	18.1	H <sub>2</sub> O <sup>+</sup> ( <sup>4</sup> A <sub>2</sub> ) → OH <sup>+</sup> ( <sup>3</sup> Σ <sup>-</sup> ) + H	17.9
		-		21.0	H <sub>2</sub> O <sup>+</sup> ( <sup>2</sup> B <sub>2</sub> ) → OH <sup>+</sup> ( <sup>1</sup> Δ) + H	~20
					or → OH <sup>+</sup> ( <sup>1</sup> Σ <sup>+</sup> ) + H	~21
O <sup>+</sup>	2.0	18.8	1.25		H <sub>2</sub> O( <sup>2</sup> B <sub>2</sub> ) → OH <sup>+</sup> ( <sup>3</sup> Σ <sup>-</sup> ) + H	17.9
Pressure induced metastable peak.						
H <sup>+</sup>	5.0	-	5.05	16.0	H <sub>2</sub> O* → H <sup>+</sup> ( <sup>1</sup> S) + OH <sup>-</sup> ( <sup>1</sup> Σ)	16.9
		-	19.5	19.6	H <sub>2</sub> O <sup>+</sup> ( <sup>2</sup> A <sub>2</sub> ) → H <sup>+</sup> ( <sup>1</sup> S) + OH( <sup>2</sup> Π <sub>1</sub> )	18.7
		-				

<sup>a</sup> electron energy 100 eV

<sup>b</sup> electron energy 50 eV

Table 2. Mass spectra of  $H_2O$  obtained in charge exchange with incident positive ions of low kinetic energy (KE) as a function of the pressure in the collision chamber.

Incident ion	KE eV	Pressure microns	Ions				
			$H_3O^+$	$H_2O^+$	$OH^+$	$m/e=16$	Q
$Ne^+$	25	2.0	(73.3)	66.7	33.3	-	0.2
	25	0.8	(21.2)	39.5	60.5	-	0.1
	25	0.1	(2.3)	14.3	85.7	-	0.2
	100	0.1	(2.8)	19.4	80.6	-	0.1
	900	0.1	(1.9)	15.3	84.7	-	0.2
$F^+$	10	0.6	(14.4)	79.7	20.3	-	3
	10	0.3	(5.9)	81.0	19.0	-	3
	10	0.1	(3.0)	79.7	20.3	-	4
	23	0.4	(6.0)	82.1	17.7	0.2	5
	23	0.2	(3.1)	82.3	17.7	-	2
	23	0.1	(1.5)	81.3	18.7	-	3
	300	0.8	(9.5)	60.6	39.1	0.3	9
	300	0.3	(3.3)	60.0	40.0	-	9
	300	0.1	(1.7)	59.7	40.3	-	10
	900	0.8	(10.9)	50.8	48.8	0.4	8
	900	0.3	(2.8)	47.2	52.2	0.6	9
	900	0.1	(1.5)	46.2	53.4	0.4	12

Table 2. (Continued)

Incident ion	KE eV	Pressure		Ions			
		microns	$H_3O^+$	$H_2O^+$	$OH^+$	$m/e=16$	Q
$Xe^{++}$	17	1.1	(54.8)	92.1	7.9	-	0.9
	17	0.6	(19.2)	88.4	11.6	-	0.8
	17	0.1	-	85.7	14.3	-	0.7
	35	1.2	(55.1)	84.2	15.8	-	1
	35	0.5	(16.0)	76.4	23.6	-	1
	35	0.1	(3.7)	74.1	25.9	-	1
	100	1.2	(28.8)	65.9	33.8	0.3	4
	100	0.6	(8.5)	58.2	41.4	0.4	3
	100	0.1	(1.9)	54.8	45.2	-	4
	900	1.2	(28.7)	61.3	38.3	0.4	5
	900	0.6	(7.5)	53.9	45.7	0.4	5
	900	0.1	(1.5)	50.2	49.3	0.5	5
$Ar^+$	12	0.1	(2.9)	100.0	0.0	0.0	8
	100	0.1	(1.3)	98.7	1.3	0.0	11
	900	0.1	(1.6)	97.8	2.2	0.0	6
$Kr^+$	11	0.1	(2.9)	100.0	0.0	0.0	23
	100	0.1	(1.4)	99.8	0.2	0.0	11
	900	0.1	(1.4)	99.4	0.6	0.0	10
$CO_2^+$	22	0.1	(1.9)	100.0	0.0	0.0	11
	100	0.1	(1.8)	99.7	0.3	0.0	11
	900	0.1	(1.4)	99.3	0.7	0.0	8

Table 3. Relative abundance in % of molecule ions, p, and "parent-  
-plus-one", p+1, from CH<sub>3</sub>OH and CH<sub>3</sub>NH<sub>2</sub> after charge  
exchange with incident positive ions of low kinetic energy  
(KE) as a function of the pressure in the collision chamber.  
The p+1 ions are not included in the normalization.

CH <sub>3</sub> OH					CH <sub>3</sub> NH <sub>2</sub>				
Incident ion	KE eV	Pressure $\mu$	p	p+1	Incident ion	KE eV	Pressure $\mu$	p	p+1
Ne <sup>+</sup>	18	1.8	3.2	54.2	He <sup>+</sup>	25	0.7	4.0	8.6
	18	0.9	2.1	15.5		25	0.3	1.5	2.5
	18	0.3	1.0	4.8		25	0.1	1.0	1.0
	18	0.1	0.7	3.3		18	0.7	3.6	15.3
F <sup>+</sup>	30	1.3	1.2	48.0	Ne <sup>+</sup>	18	0.3	1.4	4.0
	30	0.9	1.0	18.7		18	0.1	1.4	2.0
	30	0.3	1.6	7.0		36	0.7	3.3	13.1
	30	0.1	1.5	2.2		36	0.3	1.8	4.3
Ar <sup>+</sup>	15	1.8	0.6	110.0	F <sup>+</sup>	36	0.1	1.0	3.0
	15	0.9	0.4	25.7		20	0.7	2.6	13.6
	15	0.3	0.1	4.8		20	0.3	1.1	4.4
	15	0.1	0.0	2.0		20	0.1	0.4	2.3
Kr <sup>+</sup>	20	1.8	0.3	108.0	Ar <sup>+</sup>	25	0.7	0.7	8.9
	20	0.9	0.3	27.5		25	0.3	0.3	3.4
	20	0.3	0.4	5.5		25	0.1	0.5	1.9
	20	0.1	0.3	2.7		35	0.7	0.8	9.8
N <sub>2</sub> O <sup>+</sup>	20	1.8	1.1	87.0	Xe <sup>+</sup>	35	0.3	0.3	3.4
	20	0.9	1.0	23.0		35	0.1	0.2	1.7
	20	0.3	1.1	6.5					
	20	0.1	1.2	3.5					

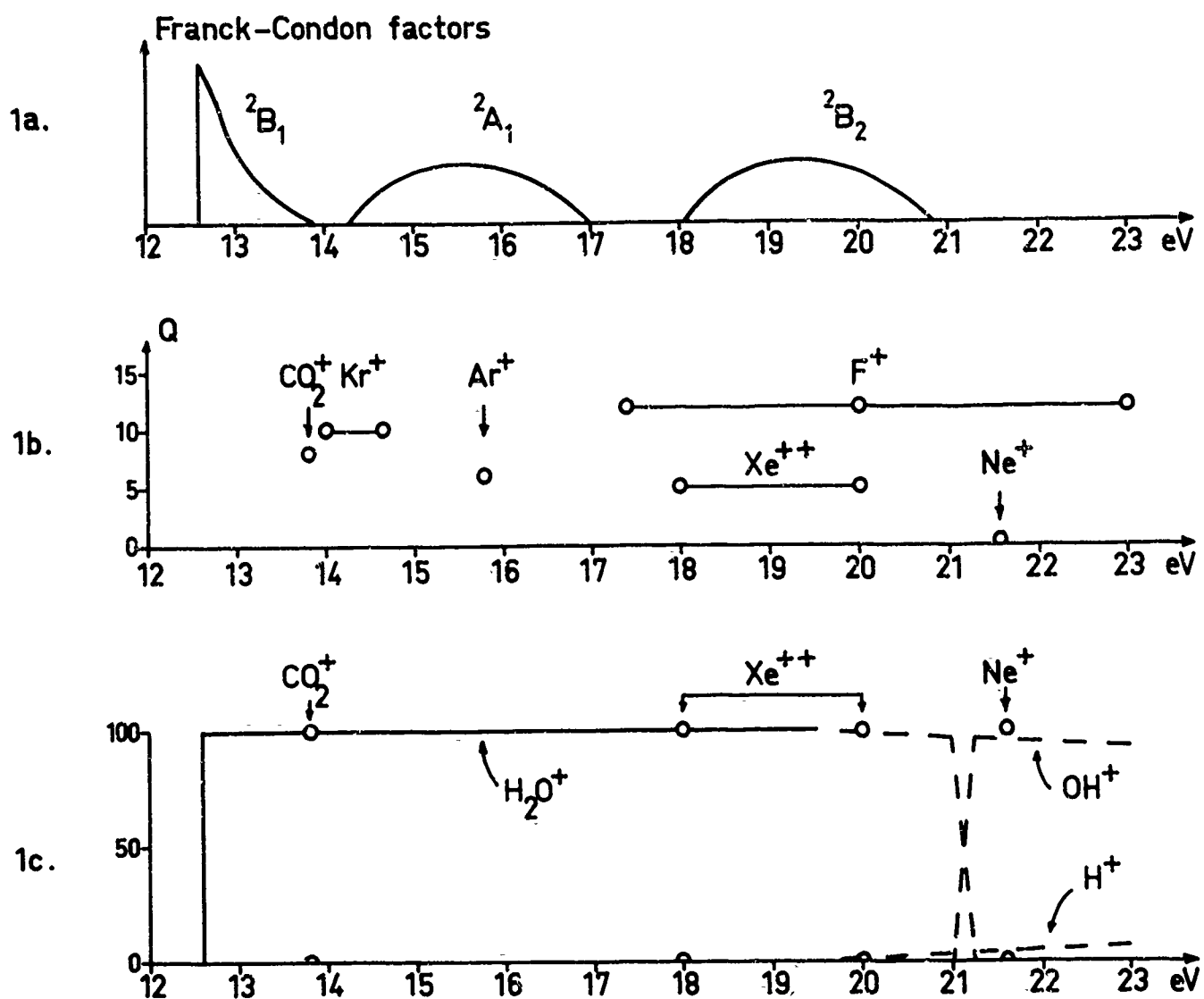


Fig. 1. a) Estimated Franck-Condon factors for ionization of  $\text{H}_2\text{O}$ .  
 b) Relative cross sections for charge transfer between different positive ions and  $\text{H}_2\text{O}$ .  
 c) Mass spectrum of  $\text{H}_2\text{O}$  as a function of energy (eV).

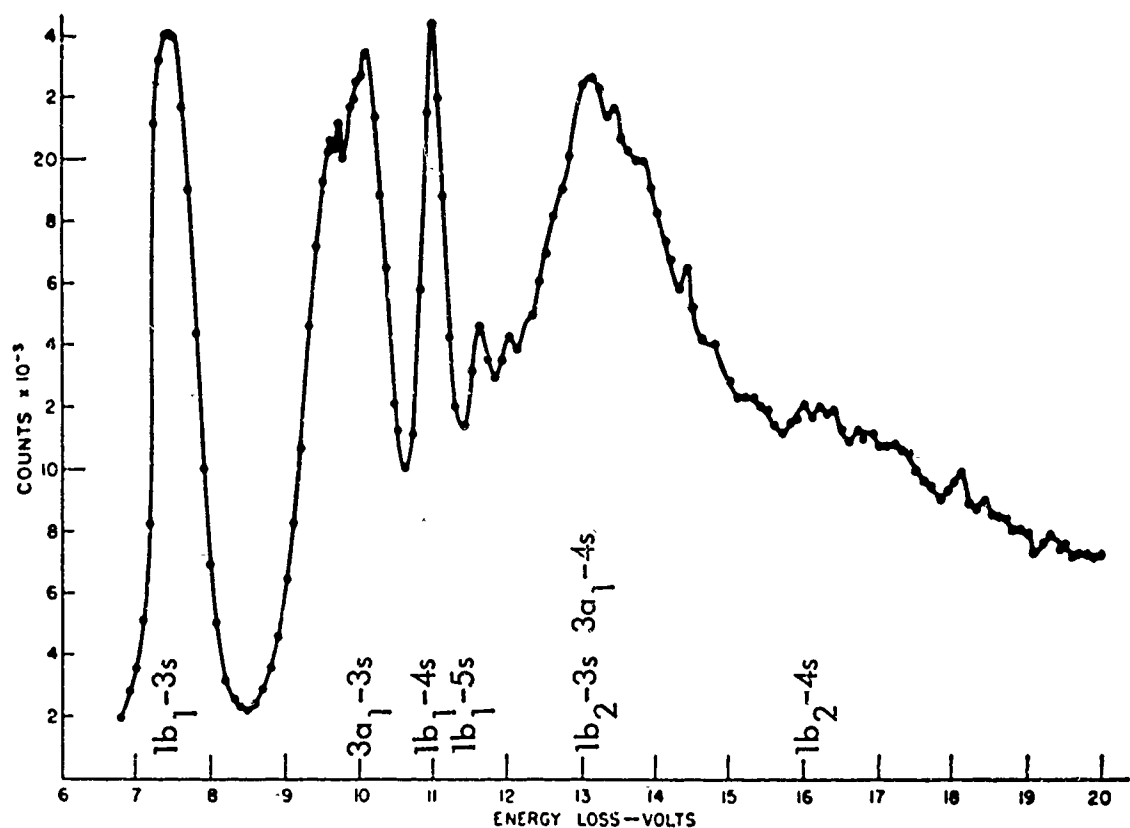


Fig. 2. Energy loss spectrum of H<sub>2</sub>O obtained by Skerbele and Lassetre [19]. The transitions discussed in the present paper are included in the figure.



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13. ABSTRACT			
<p>The ionization of <math>H_2O</math> was investigated, using charge exchange in a double mass spectrometer. The breakdown graph was constructed. A break in the electron impact ionization efficiency curve is explained as being due to preionization, as its explanation as being due to an ion-molecule reaction between <math>H^+</math> ions and <math>H_2O</math> seems to be less probable. The appearance potential of <math>OH^+</math> was found to be considerably higher with charge exchange than when electron impact was used, which agrees with our earlier finding that intercombination transitions seem to be more strictly forbidden in charge exchange than in electron impact.</p> <p><math>CH_3NH_2</math> and <math>CH_3OH</math> were investigated, using charge exchange at elevated pressures. The breaks in the ionization efficiency curves for these molecules are discussed and ascribed to preionization or secondary processes.</p>			

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Charge exchange						
Electron impact						
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CH <sub>3</sub> NH <sub>2</sub>						
CH <sub>3</sub> OH						
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